TITLE:

Study on Surface Electricity. (XX) : On Capacity Measurement of Dropping Mercury Electrodes by Resonance Method. (2)

AUTHOR(S):

Watanabe, Akira; Tsuji, Fukuju; Ueda, Shizuo

CITATION:

Watanabe, Akira ...[et al]. Study on Surface Electricity. (XX) : On Capacity Measurement of Dropping Mercury Electrodes by Resonance Method. (2). Bulletin of the Institute for Chemical Research, Kyoto University 1956, 34(1-2): 1-9

ISSUE DATE:

1956-03-30

URL:

http://hdl.handle.net/2433/75547

RIGHT:

京都大学学術情報リポジトリ
KURENAI 紅
Kyoto University Research Information Repository

Study on Surface Electricity. (XX)

On Capacity Measurement of Dropping Mercury Electrodes by Resonance Method. (2)

Akira WATANABE, Fukuju TSUJI and Shizuo UEDA*

(Tachi Laboratory)

Received February 2, 1956

The differential double layer capacities of mercury-salt solution interfaces were determined, using the resonance method described in the preceding paper.

The shapes and positions of the capacity-bias potential curves obtained depended chiefly on the nature of anions in solution and very little on the nature of cations in the anodic region as well as in the electrocapillary maximum region. The potentials at the peaks of humps near electrocapillary maxima were independent of the nature of cations, and had almost the same values for given anionic species except sulfates. The capacities at humps of various anions could be arranged in a series similar to that of solubilities of the corresponding mercurous salts. By using a simple model of electrostatic condenser, the dielectric constant between mercury surface and outer Helmholtz plane was calculated to be about 7.5, which was considerably saturated value for the dielectric constant of water.

The behaviour of differential double layer capacity of a mercury-salt solution interface provides so much accurate knowledge of the interfacial double layer structure that attention has been paid on it by various authors.[1] As this quantity depends upon the excess charge (e. g. ions and dipole molecules of solvent etc.) in solution side of the interface, it is a function of polarizing potential (bias voltage) as well as of ionic species in solution and of the character of solvent, which distinguishes its behaviour from that of an ordinary electrostatic condenser of constant capacity.[2] We can, therefore, estimate the distribution of charged particles in solution phase of double layer and other important natures by the measurement of this quantity.

The above considerations forced us to many trials of the measurement, e. g. "Impedance Matching Method and Resonance Method, both using U-effect II"[1] and "Resonance Method using Dropping Mercury Electrode"[3], and from a pile of experimental studies, we got a conclusion that the last mentioned was the most accurate one among them.

This paper contains the results of the interfacial double layer capacity measurements at bias voltage from 0 to -2.0 V with various mercury-salt solution interfaces and their explanation from the viewpoint of double layer structure.

---

*渡辺昌，辻福寿，上田静男

Table 1. Differential double layer capacity of mercury-1N salt solution interfaces.

	Acids			K-salts							
φ (v)	HCl	$\frac{1}{2}H_2SO_4$	HNO_3	KF	KCl	KBr	KI	$\frac{1}{2}K_2SO_4$	KNO_3	$\frac{1}{2}K_2CO_3$	$KClO_3$
0.0		104.58	91.72					68.52			48.54
-0.1	100.39	44.01	49.69	42.26				46.19	31.68		33.50
-0.2	49.56	33.45	37.90	32.23	71.68	73.34		45.65	28.36	61.20	31.90
-0.3	39.01	29.52	32.19	28.84	45.45	61.80	73.74	47.62	25.09	36.99	30.48
-0.4	41.98	29.96	27.08	32.18	51.27	60.06	89.47	45.08	25.31	31.28	28.50
-0.5	44.39	34.65	24.17	29.14	48.17	52.50	62.88	37.80	26.06	25.83	27.51
-0.6	38.38	35.92	22.90	26.55	37.99	34.42	40.40	30.73	30.03	22.47	29.09
-0.7	31.06	30.61	23.90	22.29	29.94	25.00	27.80	27.64	33.27	20.60	30.32
-0.8	21.47	26.50	28.01	19.95	20.70	18.31	21.07	23.81	32.87	18.30	28.97
-0.9	18.60	21.17	31.73	18.25	18.13	16.66	19.68	21.02	29.17	18.68	25.15
-1.0	16.52	19.18	35.05	17.35	18.43	16.13	20.81	18.78	23.53	17.57	22.46
-1.1	15.67	17.03	31.18	17.44	17.52	16.43	19.69	16.95	19.88	17.39	18.37
-1.2	15.72	16.58	25.11	17.01	17.69	16.99	21.42	17.08	16.78	17.28	17.30
-1.3	18.26	16.28	24.25	16.68	18.03	17.42	23.12	16.84	15.21	18.22	15.59
-1.4		15.90		17.56	18.15	18.78	25.23	17.29	15.18	19.75	16.17
-1.5		16.55		19.55	18.85	19.54	35.69	17.00	15.49	21.58	16.85
-1.6				19.09	20.87	20.51		17.72	16.61	22.54	16.49
-1.7				20.74	22.15	23.59		18.91	17.24	23.94	18.20
-1.8				22.39	21.99			20.14	17.64	31.78	15.73
-1.9				24.62	30.80			21.70	22.54		
-2.0				42.32				21.98			
φ_{max}	-0.57	-0.7	-0.92	-0.49	-0.54	-0.48	-0.4	-0.61	-0.73	-0.41	-0.7
$t°$ C	26	23	23	22	22	23	22	23	23	24	26

	Na-salts					NH_4-salts			
φ (v)	NaCl	NaBr	$\frac{1}{2}Na_2SO_4$	$NaNO_3$	$\frac{1}{2}Na_2CO_3$	NH_4Cl	NH_4Br	$\frac{1}{2}(NH_4)_2SO_4$	NH_4NO_3
0.0			93.58					53.78	
-0.1	109.47		46.21	36.14		84.20		45.65	31.37
-0.2	54.82	67.86	43.18	29.82	69.16	48.73	73.44	44.87	25.97
-0.3	41.98	56.48	47.33	26.69	42.29	44.16	55.15	46.05	24.88
-0.4	47.01	53.72	39.62	25.58	30.29	49.22	53.63	46.63	24.08
-0.5	50.21	48.46	31.17	29.64	28.10	46.68	53.63	38.73	26.56
-0.6	36.91	34.64	29.49	36.92	24.66	35.68	38.76	33.03	30.10
-0.7	29.10	24.16	22.02	44.72	20.74	27.23	26.40	29.35	34.33
-0.8	20.67	18.72	20.83	41.64	18.36	21.35	20.76	25.38	33.82
-0.9	17.18	25.03	17.80	39.41	18.65	18.58	17.67	21.12	28.63
-1.0	16.74	24.92	18.31	27.06	18.14	16.74	16.94	19.75	23.27
-1.1	15.72	24.66	16.17	22.02	17.75	18.05	17.04	18.21	18.98
-1.2	15.55	25.16	16.19	18.51	18.33	18.25	17.60	18.19	16.84
-1.3	15.91	17.21	16.10	17.97	18.37	18.02	20.24	18.37	16.95
-1.4	16.94	18.32	16.83	16.84	18.67	18.94	21.91	19.03	16.91
-1.5	17.11	18.99	16.76	18.48	21.31	20.07	23.41	18.85	17.81
-1.6	18.82	19.04	17.01	18.93	21.64	20.66	27.21	20.10	18.35
-1.7	18.68	36.40	16.85	18.02	21.22	23.05	54.00	22.59	20.50
-1.8	19.56		19.12	19.14	27.39	27.02		23.07	
-1.9	34.53		20.01	19.16	38.48			25.57	
-2.0			24.47					32.74	
φ_{max}	-0.54	-0.5	-0.55	-0.7	-0.41	-0.53	-0.37	-0.63	-0.71
$t°$ C	26	25.5	24	23	24	26	23	22	23

1. EXPERIMENT

Differential double layer capacities were obtained as functions of d. c. bias voltage

by resonance method using dropping mercury electrodes immersed in the salt solution examined. We shall not give detailed description of measurement here.[3]

For systematic survey of the influence of anionic and cationic species in solution on measured capacity values, various salt solutions of concentration of one normal were used.

2. RESULTS

Table 1 shows the differential double layer capacity data (C_0) as functions of d. c. bias voltage (φ). For the sake of brevity details of the experimental conditions are not included, the outline of which is as follows :[8]

$$\varphi = 0 \sim -2.0\,\mathrm{V}, \quad W = 7 \sim 11\,\mathrm{mg},$$
$$A = 0.03 \sim 0.04\,\mathrm{cm}^2, \quad T = 1 \sim 2\,\mathrm{sec},$$
$$f = 200 \sim 500\,\mathrm{cps}, \quad E = 7.4\,\mathrm{mV}\ (\mathrm{a.\ c.}),$$
$$L = 70 \sim 250\,\mathrm{mh}, \quad C = 0.5 \sim 6.0\,\mu\mathrm{F}.$$

3. SYSTEMATIC SURVEY OF CAPACITY CURVES

The differential double layer capacities as functions of bias voltage, as are shown in Table 1, have the following common features :

(1) They are much larger in anodic region ($\varphi - \varphi_{max} > 0$) than in cathodic region ($\varphi - \varphi_{max} < 0$), and there are steep rises in extreme anodic polarization.

(2) There are flat minima of about 16 μF/cm^2 in cathodic region.

(3) Humps are seen, in general, near electrocapillary maximum regions ($\varphi \fallingdotseq \varphi_{max}$).

(4) The effect of cations is not specific in cathodic regions as well as in anodic regions.

(5) The effect of anions is specific, especially in anodic as well as in electrocapillary maximum regions.

(6) There are sharp enhancements in extreme cathodic regions. These are, of course, ascribed to electrolyses, and we shall not discuss them here. They are called by D. C. Grahame, "Pseudo-capacities".

These properties become more evident when we see the C_0-$\boldsymbol{E}$ curves in Figs. 1, 2, 3, 4 and 5.[9] Each of the first four figures contains curves of the solutions of the same cationic but different anionic species. It is noticed that the curves in the same figure have diverse shapes and positions, owing to the difference of anionic species. On the contrary, if we bring together the curves of the solution of the same anionic but different cationic species, the curves almost coincide in each group. This is clearly shown by the last figure, where only those for chlorides are indicated, the other groups showing the same tendency, although they are not given here.

The characteristic features summarized above are quite in accord with D. C. Grahame's descriptions.[5] We shall discuss them by dividing the polarization in three

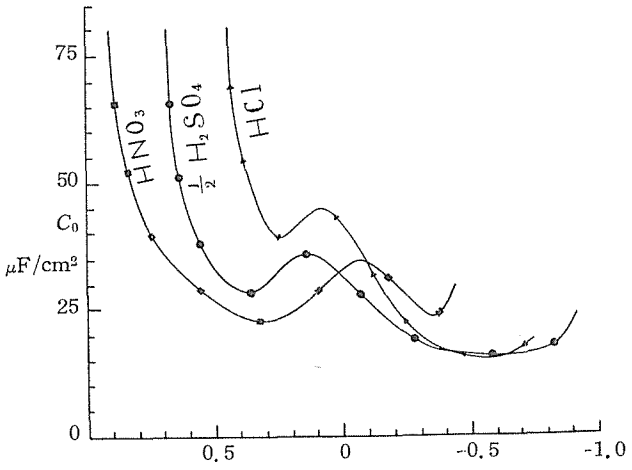

Fig. 1. Acids

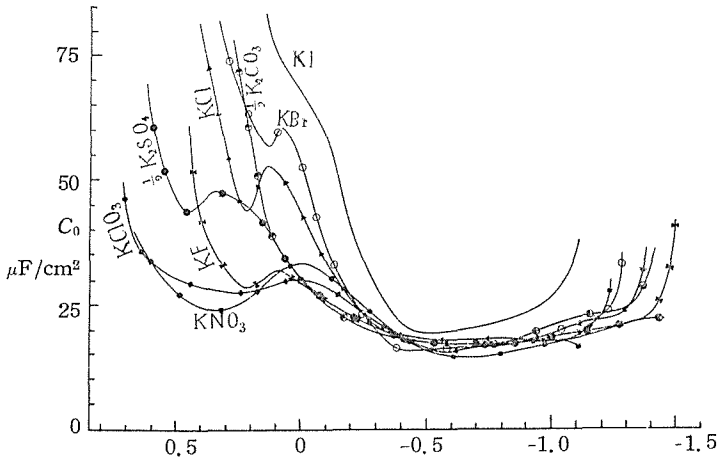

Fig. 2. K-salts.

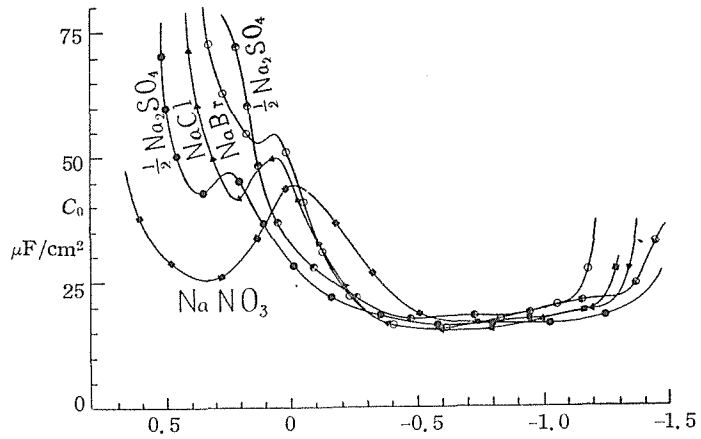

Fig. 3. Na-salts.

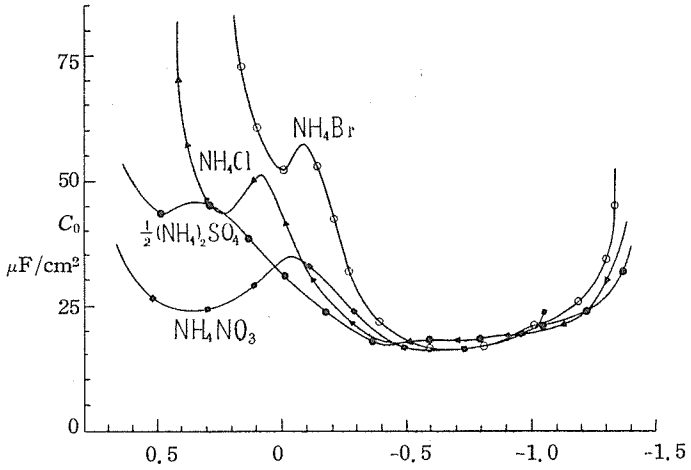

Fig. 4. NH_4-salts.

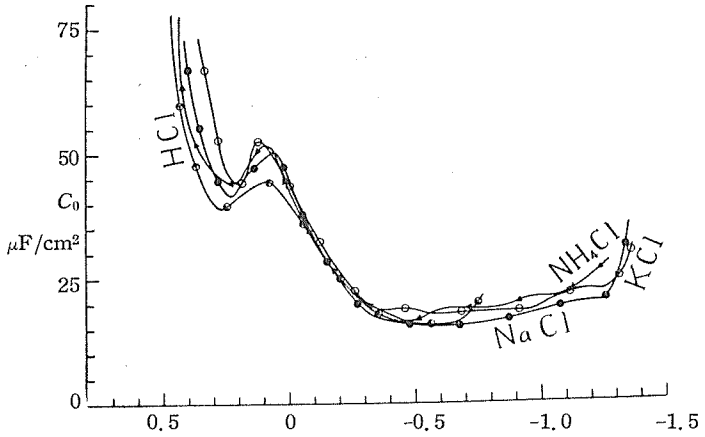

Fig. 5. Chlorides

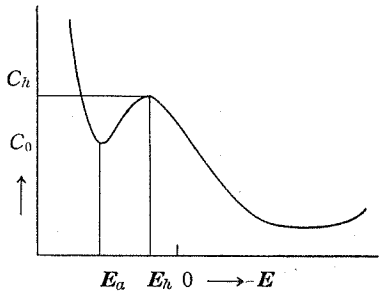

Fig. 6.

regions, i. e. cathodic, anodic and electrocapillary maximum (or zero) regions. Figure 6 shows a representative curve, where C_h is the capacity value at hump, E_h the potential giving maximum of the hump and E_a that where anodic rise begins. In Table 2 are

shown the values of these characteristic quantities obtained from Table 1.

Table 2. Several properties at humps of differential capacity curves near electrocapillary maxima.

Cationic species / Anionic species	H			K			Na			NH_4		
	E_h (v)	C_h (μF/cm^2)	E_a (v)	E_h	C_h	E_a	E_h	C_h	E_a	E_h	C_h	E_a
I												
Br				0.07	60.5	0.12	0.06	54.5	0.13	-0.08	58.0	0.00
Cl	0.08	44.5	0.25	0.10	52.0	0.20	0.05	50.0	0.23	0.09	51.5	0.23
F				0.08	32.0	0.21						
$\frac{1}{2}SO_4$	0.13	35.5	0.37	0.32	48.0	0.45	0.25	47.0	0.36	0.34	45.5	0.47
NO_3	-0.07	35.0	0.30	-0.03	33.5	0.35	0.00	44.5	0.34	-0.04	35.0	0.38
$\frac{1}{2}CO_3$												
ClO_3				-0.03	30.0	0.22						

(i) Anodic region ($E > E_a$)

The double layer capacities at extreme anodic polarization are said by D. C. Grahame to be influenced specifically by anionic species in solution.[4] Anions can be arranged in the same series of ascending magnitudes of these capacity values, as that of ascending bond strengths of the corresponding mercurous salts of the anions. This is satisfied also by our experimental results. The anionic series in increasing capacity in this region is, for every cationic species,

$$NO_3' < ClO_3' < \tfrac{1}{2}SO_4'' < F' < Cl' < Br' < \tfrac{1}{2}CO_3'' < I'$$

Table 3. Physical properties of individual anion

Anion (X)	I′	Br′	Cl′	F′	$\frac{1}{2}SO_4''$	ClO_3'	NO_3'	$\frac{1}{2}CO_3''$
Difference in Lattice Energy $U_{AgX}-U_{NaX}$ (cal)	39.1	31.4	25.6	9.3	11.5		10.5	17.9
Solubility of Corresponding Mercurous Salt	10^{-8}	10^{-7}	10^{-5}		$10^{-3.5}$			$10^{-3.5}$

It is clear from column 3 of Table 3 that this series is the same as that of decreasing solubility of corresponding mercurous salts of respective anions, which measures the bond strength between mercury and corresponding anions.

D. C. Grahame concluded from this fact that anions in this region were directly adsorbed by mercury surface by nearly chemical bonding, giving rise to the so-called "Inner Helmholtz Plane", which gave high intrinsic capacity and explained high values of double layer capacities in this region compared with those in cathodic region, where cations were adsorbed indirectly maintaining their hydration sheaths.

This model proposed by D. C. Grahame also gives explanation of the specific con-

tribution of anionic species to capacity behaviour in this region, because, if anions were not dehydrated, they would not show such evident specificity in this region in spite of their different ionic radii. There is, of course, a diffuse double layer of Gouy, which extends from the first hydrated ions (Outer Helmholtz Plane) into the bulk of solution. However, its capacity being very large, i. e. hundreds of $\mu F/cm^2$, and laying itself in series to the inner layer capacity, it does not contribute effectively to the capacity behaviour in such concentrated solutions (1N).

(ii) Cathodic region ($E<0$)

Cationic adsorption prevails in this region. Cations are generally smaller than anions, and the triangular structures of water molecules orientated around a cation, in addition, have negative pole of electricity faced to it. For these reasons they are generally more difficult to be dehydrated than anions. We can say from this that cations are adsorbed by mercury surface by Coulombic force through dielectricum of water molecules.

The (integral) electrical capacity of a plane condenser of unit area is given by

$$C_0 = \epsilon/4\pi d ,$$

where ϵ is the dielectric constant of medium, and d the distance of the plates of the condenser. If we substitute the values, $C_0 = 16\ \mu F/cm^2$ and $d = 2r_w + r = 4.13$Å, where r_w and r are the radii of water molecule and cation (here for instance 1.33 Å for potassium ion), we get

$$\epsilon \fallingdotseq 7.5.$$

The dielectric constant of water in direct contact with an ion in solution is very low, owing to dielectric saturation in high field strength, which is about 1.6×10^8 V/cm at distance of 3 Å from the center of 1-valent ion. If we suppose the saturation to be due to loss of orientation freedom of water dipoles, the dielectric constant in such a strong field must decrease to $n^2 = 4.13$.[10]

If the ion is brought to the surface of opposite charge, the field strength between them becomes still more strong, due to concentration of faradaic fluxes. We can therefore, suppose that the dielectric constant saturates also in this case. It must have the value of about 4.13. It is noticed that the above value of dielectric constant of water at interface obtained from capacity data is in considerably good agreement with this consideration, when the rough model of the double layer structure in cathodic region is taken into account.

(iii) Zero region ($E\fallingdotseq0$)

The capacity behaviour in this region is influenced specifically by anionic species in solution as well. This is evident from the $C_0 \sim \varphi$ curves and Table 3. Although no regularity is observed when the characteristic quantities of humps are compared between

salt solutions of the same anionic but different cationic species, there is definite regularity among those having the same cationic but different anionic species.

This region is very important in the sense that it is intimately connected with absolute potentials of electrodes. However, the electrocapillary maximum potential must not be confused with this absolute potential, because there may be a potential difference due to orientation of water and other dipoles etc. It is only a point where the surface charge of mercury is zero.[2,4]

The capacity behaviour in this region attracts our attention very much, because there is a noticed enhancement of capacity value in almost every case. Nevertheless, nobody has ever examined this phenomenon in detail. Its systematic study gives us some interesting conclusion about this yet unsolved problem.

In the first place, the potential of maximum of hump is nearly zero in every case, except two-valent sulfate ion (Table 3). In other words, the humps occur near electrocapillary maximum. This suggests that the humps may due either to rarefaction of surface charge of mercury or diminishment of double layer field.

We must notice here that not the population of charged particles in solution phase of the double layer, but the *excess* charge, is rare in this region. Therefore, if the hump is attributed to the former cause, it must not be explained from ion-ion interaction but from mercury-ion interaction.

In relation to the second assumed cause, we must pay some attention about absolute potential. From the theoretical consideration of electrode kinetics, reversible reduction must occur within $-0.5/(1-\alpha)n$ V from absolute zero potential.[11] On the other hand, polarographic study shows that the experimental half-wave potentials of most reversible reduction of metallic ions seem to lie near electrocapillary maximum. This fact suggests that the absolute zero potential lies in the region considered here, although electrocapillary maximum may not strictly coincide with it.

In the second place, if we examine the values of C_h in Table 3, we notice a very interesting fact, that, if they are arranged in ascending magnitudes, following anionic series are obtained:

K-salts ;	$ClO_3' < F' < NO_3' < \frac{1}{2}SO_4'' < Cl' < Br' < (I')$
Na-salts ;	$NO_3' < \frac{1}{2}SO_4'' < Cl' < Br'$
NH_4-salts ;	$NO_3' < \frac{1}{2}SO_4'' < Cl' < Br'$
acids ;	$NO_3' < \frac{1}{2}SO_4'' < Cl'$

As all series are the same in spite of the difference of cationic species, we can conclude that this quantity is specifically dependent on anionic species in solution.

Column 2 of Table 2 shows the differences in lattice energies of Na- and Ag-salts of the same anions. As they give the measures of the deformabilities of anions,[7] it is very interesting to notice that they are arranged in the same series as the upper-mentioned series of C_h. It is, of course, not unexpected that the double layer capac-

ity is dependent on the dielectric properties of the chemical species present at interface.

The authors express their gratitude to Prof. Dr. I. Tachi for his continued interest and encouragement. Thanks are also due to Messrs. T. Tabata, T. Tosa and A. Murakami in this laboratory for their assistance in performing the experiments.

REFERENCES AND NOTES

(1) S. Ueda, A. Watanabe and F. Tsuji, This Bulletin, **24**, 12 (1951); **25**, 30 (1951); **29**, 32 (1952); **32**, 54, 62 (1954) and references in them.
(2) A. Watanabe and S. Ueda, *J. electrochem. Soc. Japan*, **20**, 247, 308, 358, 419 (1952).
(3) A. Watanabe, F. Tsuji and S. Ueda, This Bulletin, **33**, 91 (1955).
(4) D. C. Grahame, *Chem. Rev.*, **41**, 441 (1947).
(5) D. C. Grahame, *J. Amer. Chem. Soc.*, **83**, 1207 (1941); **68**, 301 (1946).
(6) P. Delahay, *J. Amer. Chem. Soc.*, 1430 (1953). n is the number of electrons involved in the electrode reduction, and α is the transfer coefficient for the forward electrode process.
(7) Eggert, "Physical Chemistry", Constable, London, p. 374 (1932).
(8) The notations have the same meanings as in the preceding paper.[3]
(9) The potentials written in gothic style are those viz. electrocapillary maximum potentials, *i. e.* $\boldsymbol{E} = \varphi - \varphi_{max}$
(10) n is the refractivity index of water.
(11) There seems to be a mistake in consideration of P. Delahay's paper.[6] The potential of a hydrogen electrode is a relative one, and it cannot control the absolute character of other ions like their reversibility of reduction.